



Progress in Materials and Component Development for Advanced Lithium-ion Cells for NASA's Exploration Missions

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Abstract

Vehicles and stand-alone power systems that enable the next generation of human missions to the Moon will require energy storage systems that are safer, lighter, and more compact than current state-of-the-art (SOA) aerospace quality lithium-ion (Li-ion) batteries. NASA is developing advanced Li-ion cells to enable or enhance the power systems for the Altair Lunar Lander, Extravehicular Activities spacesuit, and rovers and portable utility pallets for Lunar Surface Systems. Advanced, high-performing materials are required to provide component-level performance that can offer the required gains at the integrated cell level. Although there is still a significant amount of work yet to be done, the present state of development activities has resulted in the synthesis of promising materials that approach the ultimate performance goals. This report on interim progress of the development efforts will elaborate on the challenges of the development activities, proposed strategies to overcome technical issues, and present performance of materials and cell components.

1.0 Introduction

NASA's Exploration Technology Development Program (ETDP) Energy Storage Project, which existed from fiscal year 2006 (FY06) through FY10, was chartered with the development of advanced energy storage technologies to enable or enhance NASA's Constellation missions. Developments were specifically targeted to the requirements of three customers: Altair Lunar Lander, Extravehicular Activities (EVA) spacesuit, and Lunar Surface Systems (LSS). In response to NASA's changing direction, with potential human missions to Near Earth Objects (NEOs) that may include asteroids, planets, moons, libration points, and orbiting structures, ETDP concluded at the end of FY10. The beginning of FY11 marked its transition into the Enabling Technology Development and Demonstration Program (ETDD). The Battery Development Effort now resides under the High Efficiency Space Power Systems (HESPS) Project within ETDD. Although the vehicles that will enable missions to NEOs may change, it is a certainty that high specific energy, high energy density batteries will be required to provide new capabilities to enable or enhance these missions. Until specific future missions and requirements are known, the Battery Development Effort continues to pursue the goals that were previously established to address the needs of Altair, EVA, and LSS.

Customer requirements and desires were distilled into practical performance metrics for advanced technology development. LSS customers require human-rated technologies that offer a higher degree of safety over SOA Li-ion battery systems, that are lightweight and compact, and that can sustain rovers, portable utility pallets (PUP), and other mobile systems over long duration stays on the Lunar surface. The Concept of Operations (ConOps) requires cycle lives up to 2000 deep-discharge cycles and calendar lives of up to 5 to 10 years.

The concept of a High Energy (HE) flightweight cell was developed for LSS. The HE cell offers modest advancements in specific energy over SOA in an inherently safe cell system. A suite of components under development to enable the HE cell includes cathodes, electrolytes, and safety components. Advanced and developmental separator materials that can be obtained commercially are under investigation for their potential use in the cell, as well. A SOA anode will be utilized in the cell since performance projections indicate that when combined with the potential performance of the

advanced cathode under development, a SOA carbonaceous anode possesses the specific energy and energy density required to meet the targeted cell-level performance goals. In addition, the cycle life of this class of Li-ion anodes is adequate to meet HE cycle life requirements. The use of an anode that has demonstrated performance heritage in Li-ion systems provides a level of risk reduction over developing a cell chemistry from entirely new components.

The specific energy requirements for Altair and EVA far exceed the capabilities of SOA battery systems. These customers, too, have a need for technologies that offer a higher degree of safety over SOA Li-ion battery systems. These requirements could only be addressed with the additional development of an advanced anode. Cycle life requirements for these customers are relatively benign, thus allowing the opportunity to explore different classes of anode materials. Hence, an Ultra High Energy (UHE) cell chemistry is under development to address the specific requirements of Altair and EVA applications. The developmental chemistry was chosen based on extensive studies on the best chemistry that could address the performance requirements within the budget and schedule allotted (Ref. 1). The advanced anode, when combined with other Li-ion cell components that are being developed for the HE cell, will make-up the UHE chemistry.

Once the chemistries for the HE and UHE cell were selected, Key Performance Parameters (KPPs) were developed for the HE and UHE cells with the goal of addressing Altair, EVA and LSS needs to the maximum extent possible within the constraints (budget and schedule). The KPPs are given in Table 1. These KPPs establish target criteria for the performance of cell components and integrated Li-ion cells, and project the performance that can be expected from the battery-level system that will be realized by the cells under development.

TABLE 1.—KEY PERFORMANCE PARAMETERS FOR THE HE AND UHE FLIGHTWEIGHT CELLS

Customer need	Performance parameter	State-of-the-Art	Current value	Threshold value ^a	Goal ^a
Safe, reliable operation	No fire or flame	Instrumentation/controllers used to prevent unsafe conditions. There is no non-flammable electrolyte in SOA	Preliminary results indicate a small reduction in performance using safer electrolytes and cathode coatings	Tolerant to electrical and thermal abuse such as over-temperature, over-charge, reversal, and short circuits with no fire or thermal runaway ^c	Tolerant to electrical and thermal abuse such as over-temperature, over-charge, reversal, and short circuits with no fire or thermal runaway ^c
Specific energy <u>Lander:</u> 150–210 Wh/kg 10 cycles <u>Rover:</u> 160–200 Wh/kg 2000 cycles <u>EVA:</u> 270 Wh/kg 100 cycles	Battery-level specific energy ^b [Wh/kg]	90 Wh/kg at C/10 & 30 °C 83 Wh/kg at C/10 & 0 °C (MER rovers)	160 at C/10 & 30°C (HE) 170 at C/10 & 30°C (UHE) 80 Wh/kg at C/10 & 0°C (predicted)	135 Wh/kg at C/10 & 0 °C “High-Energy” 150 Wh/kg at C/10 & 0 °C “Ultra-High Energy”	150 Wh/kg at C/10 & 0 °C “High-Energy” 220 Wh/kg at C/10 & 0 °C “Ultra-High Energy”
	Cell-level specific energy [Wh/kg]	130 Wh/kg at C/10 & 30 °C 118 Wh/kg at C/10 & 0 °C	199 at C/10 & 23 °C (HE) 213 at C/10 & 23 °C (UHE) 100 Wh/kg at C/10 & 0 °C (predicted)	165 Wh/kg at C/10 & 0 °C “High-Energy” 180 Wh/kg at C/10 & 0 °C “Ultra-High Energy”	180 Wh/kg at C/10 & 0 °C “High-Energy” 260 Wh/kg at C/10 & 0 °C “Ultra-High Energy”
	Cathode-level specific capacity [mAh/g]	180 mAh/g	252 mAh/g at C/10 & 25 °C 190 mAh/g at C/10 & 0 °C	260 mAh/g at C/10 & 0°C	280 mAh/g at C/10 & 0 °C
	Anode-level specific capacity [mAh/g]	280 mAh/g (MCMB)	330 at C/10 & 0 °C (HE) 1200 mAh/g at C/10 & 0 °C for 10 cycles (UHE)	600 mAh/g at C/10 & 0 °C “Ultra-High Energy”	1000 mAh/g at C/10 0 °C “Ultra-High Energy”

TABLE 1.—Concluded.

Customer need	Performance parameter	State-of-the-Art	Current value	Threshold value ^a	Goal ^a
Energy density Lander: 311 Wh/l Rover: TBD EVA: 400 Wh/l	Battery-level energy density	250 Wh/l	n/a	270 Wh/l “High-Energy” 360 Wh/l “Ultra-High”	320 Wh/l “High-Energy” 420 Wh/l “Ultra-High”
	Cell-level energy density	320 Wh/l	n/a	385 Wh/l “High-Energy” 460 Wh/l “Ultra-High”	390 Wh/l “High-Energy” 530 Wh/l “Ultra-High”
Operating environment 0 to 30 °C, Vacuum	Operating Temperature	–20 to 40 °C	0 to 30 °C	0 to 30 °C	0 to 30 °C

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^aAssumes prismatic cell packaging for threshold values. Goal values include lightweight battery packaging.^bBattery values are assumed at 100 percent DOD, discharged at C/10 to 3.0 V/cell, and at 0 °C operating conditions^cOver-temperature up to 110 °C; reversal 150 percent excess discharge at 1C; pass external and simulated internal short tests; overcharge 100 percent at 1C for Goal and 80 percent at C/5 for threshold value.

Components have been under development for the HE and UHE cells for well over a year now through the combination of in-house NASA and contractor efforts. Although there is still a significant amount of work yet to be done, the present state of development activities has resulted in the synthesis of promising materials that approach the ultimate goals. The following sections will elaborate on the performance of materials and cell components, the challenges of the development activities, and the proposed strategies to overcome technical issues. Data shown is preliminary data for materials that are relatively early in their development and may not yet have achieved their best performance potential. In addition, materials have not yet been optimized for performance in Li-ion cell systems.

2.0 High Energy Cell

The HE cell will consist of developmental cathode, electrolyte, safety components, and separator materials and a state-of-the-art carbonaceous anode that has demonstrated heritage in Li-ion cells.

2.1 Cathodes

Layered, transition metal oxide materials containing lithium, nickel, manganese, and cobalt (Li[LiNMC]O₂) are being developed for use in the HE and UHE cells. These cathode materials have the potential to achieve higher specific capacity than conventional Li-ion cathode materials, such as lithium cobalt oxide (LiCoO₂), and possess inherently higher thermal stability (Ref. 2). The goal is to achieve a specific capacity of 280 mAh/g at C/10 and 0 °C when discharged between 4.8 and 3.0 V. Cycle life goals for the HE cell are 2000 cycles to 80 percent of the initial capacity, hence the cathode material must be able to support such sustained cycling over > 2000 cycles.

Li[LiNMC]O₂ cathode materials have demonstrated high specific capacity on the order of 280 mAh/g between 4.8 and 2.0 V at low discharge rates on the order of C/20 and 20 °C (room temperature). However, these operating conditions are quite benign. Discharge rates of between C/10 and C/2 are required by the target applications, but because the materials suffer from low power density, capacity delivered at practical rates is significantly lower than at C/20. Currently, representative developmental materials demonstrate approximately 96, 84, and 67 percent of their C/20 room temperature capacity when cycled between 4.8 and 3.0 V at C/10, C/5 and C/2, respectively. In addition, the occupation of Li⁺ sites in the cathode by transition metal elements interferes with Li⁺ ion diffusion.

Figure 1 shows the test results of a representative coin cell containing developmental cathodes designated “V2CA”, synthesized by NEI Corporation under contract with NASA (Refs. 3 to 8). Tests were performed in 2032-type coin cells with a Li metal counter electrode, an electrolyte formulation of 1.0 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate:diethyl carbonate:dimethyl carbonate (EC:DEC:DMC) in a 1:1:1 ratio by volume, and a Tonen Setela E20 separator. Ten cycles are shown at C/10 charge and C/10 discharge rates while cycling at 23 °C (these cycles were preceded by formation cycling at C/20). On the first cycle following formation, 248 mAh/g was delivered between 4.8 and 2.0 V. 206 mAh/g was delivered to 3.0 V, a difference of 42 mAh/g. Over ten cycles, this cell and other cells made from the same electrodes retained an average of 63 percent of their initial C/10 capacity when discharged to 3.0 V, which is the equivalent of about 4 percent loss per cycle. Since these cells were cycled versus a Li metal anode, an increased rate of capacity fade is likely to have occurred than would have occurred in a full-cell configuration versus a Li-ion intercalation-type anode.

The Li[LiNMC]O₂ cathode material that has demonstrated the highest initial specific capacity of the materials under development in the ETDP project to date is Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂, developed by the University of Texas at Austin under contract with NASA (Refs. 9 to 18). It possesses a slightly different stoichiometry than the “V2CA” material discussed above. Representative voltage versus specific capacity curves for Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ materials synthesized by the University of Texas at Austin are shown in Figure 2. This material demonstrates 269 mAh/g at a C/10 discharge rate and 23 °C on its first cycle after formation when discharged from 4.8 to 2.0 V. A specific capacity of 252 mAh/g is delivered to a 3.0 V cut-off.

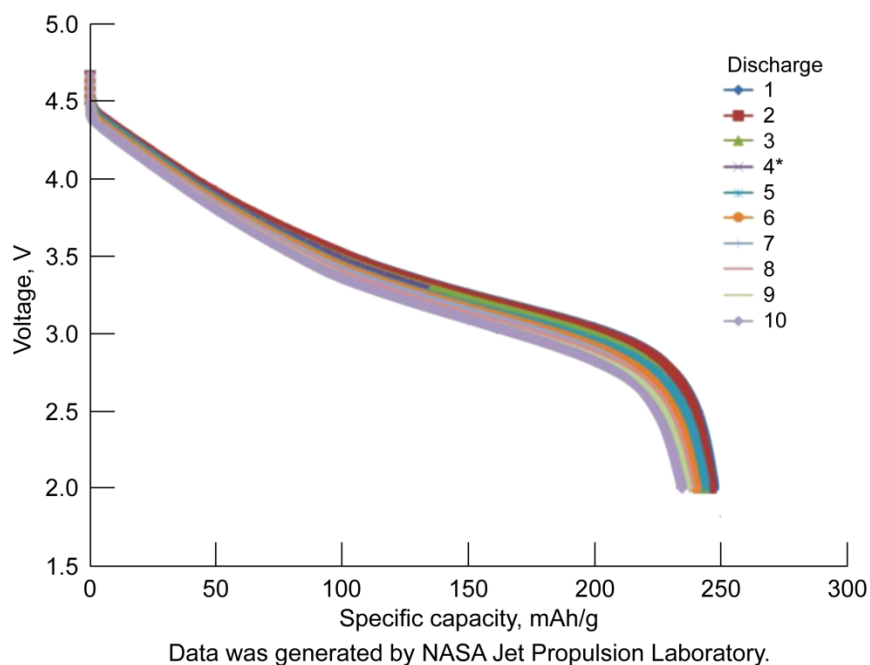


Figure 1.—Discharge curves of an NEI Corporation Li[LiNMC]O₂ cathode at C/10 and 23 °C.

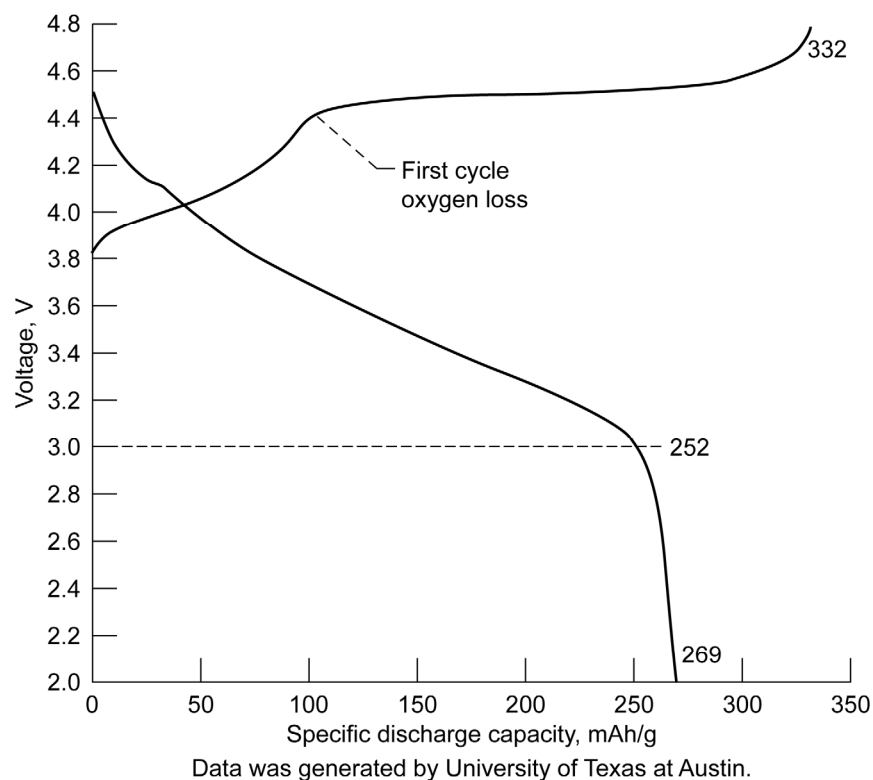
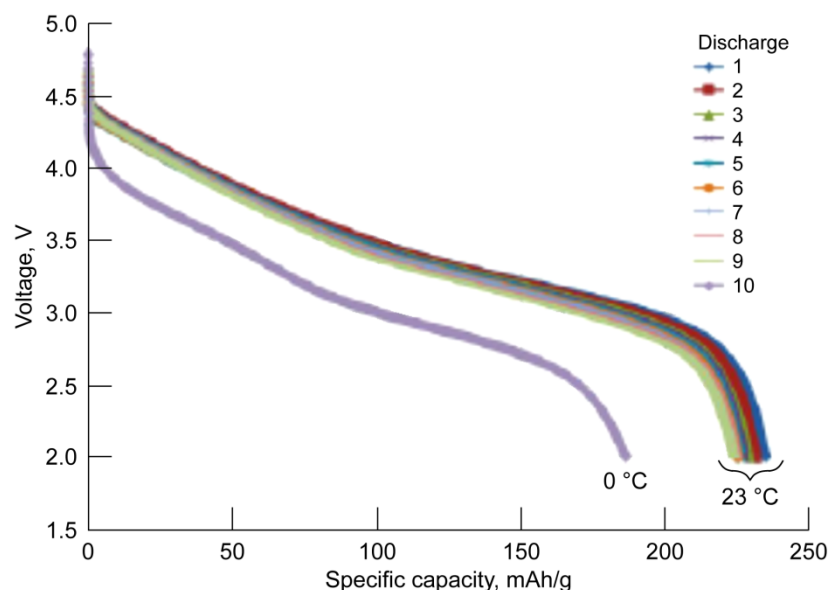


Figure 2.—First cycle charge and discharge capacity of a University of Texas at Austin $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ cathode at C/10 and 23 °C.

The $\text{Li}[\text{LiNMC}]\text{O}_2$ class of materials exhibits significant capacity below 3.0 V. The use of a DC-DC converter in the final battery system is a possible solution to make use of useable capacity below voltages that are acceptable for power quality. Mass and conversion efficiency penalties of the convertor must be traded against the specific energy benefits of the advanced cathode/cell/battery system, when limited to useable voltages without the use of a converter, to determine the net benefits and impacts on specific energy of the final system.

$\text{Li}[\text{LiNMC}]\text{O}_2$ cathodes suffer from poor kinetics at low temperatures, which results in a loss of 30 to 50 percent of room temperature capacity when the materials are operated at 0 °C. Figure 3 shows representative results of coin cell testing of a developmental cathode versus a Li metal counter electrode while discharging at a C/10 rate and 23 °C for 9 cycles. Testing was conducted on the same electrode material (but in different cells constructed in the same manner) as the cell in Figure 1. On the tenth cycle, the cell was charged at 23 °C and discharged at 0 °C. On the ninth cycle of operation at 23 °C, the cathode delivered 167 mAh/g to 3.0 V. On the tenth cycle (at 0 °C), only 101 mAh/g was delivered to the same voltage, a loss of 40 percent. Capacity loss at 0 °C is reversible and fully-recoverable when cells are returned to operation at higher temperatures (23 to 30 °C). While there is still development work to be done to ensure these classes of cathode materials can practically operate under the desired conditions, these materials have the promise to be an enabling cathode chemistry for the HE and UHE cell if these challenges can be overcome.

Technology challenges that are being addressed through cathode development include high specific capacity at practical discharge rates and voltages and at low temperatures, high tap density (high mass per unit volume), low first-cycle irreversible capacity loss, and low irreversible oxygen loss.



Data was generated by NASA Jet Propulsion Laboratory.

Figure 3.—Specific capacity of an NEI Corporation Li[LiNMC]O₂ cathode at 23 and 0 °C.

High specific capacity at practical discharge rates is being addressed by varying the stoichiometry of the cathode constituent materials to determine the optimum chemical formulation and by reducing the particle sizes of the materials. Experimentation with different synthesis methods is being pursued in order to produce materials with physical properties such that specific capacity is retained on the production scale. Synthesis methods that facilitate the incorporation of inert oxide and phosphate coatings, such as aluminum oxide (Al₂O₃), ruthenium oxide (RuO₂), aluminum phosphate (AlPO₄), and lithium metal phosphate, that have the potential to enhance rate capability, improve capacity retention, and increase discharge capacity, are also being explored (Refs. 15 and 16). Coating cathode particles with lithium metal phosphate can also lead to improvements in the thermal stability of the cathode, as discussed in Section 2.3 Safety Components.

Trials with different synthesis methods can also reveal avenues to yield higher tap density (Ref. 14). The tap density of developmental materials shown in Figures 1 and 3 is currently in the range of approximately 0.9 to 1.1 g/cc. This value must be approximately double in order to facilitate their formation into electrodes of practical thicknesses. Cathode synthesis methods are being varied to optimize the properties that can improve specific energy and the ability of the cathode powders to be cast into electrodes. Experimentation with techniques such as carbonate precipitation synthesis and non-destructive mixing has resulted in higher tap densities on the order of 1.7 g/cc for the materials shown in Figure 2. This new synthesis method allows for good control of the morphology of the materials, resulting in better electrochemical performance.

All of the cathode materials discussed thus far have pristine uncoated surfaces. Surface modification of the cathode powder particles through the use of coatings to improve cathode-electrolyte interfacial properties is being pursued for the next generation of materials we are developing. These techniques have the potential to reduce first-cycle irreversible capacity loss, enhance rate capability, improve capacity retention, and increase discharge capacity (Refs. 17, 19, and 20). Irreversible capacity losses of between 40 and 100 mAh/g have been observed on the first cycle among variants of the development cathode materials and are attributed to the evolution of oxygen gas at about 4.5 to 4.6 V on the first charge. Evidence of gas evolution is seen in materials from both the University of Texas at Austin and NEI Corporation, as indicated in Figure 2 and 4, respectively. Figure 4 shows five formation cycles (C/20 charge, C/20 discharge) for a representative sample cathode developed by NEI Corporation, (tested in coin cells versus Li metal). A 73 mAh/g difference is observed between the first and second charge capacity.

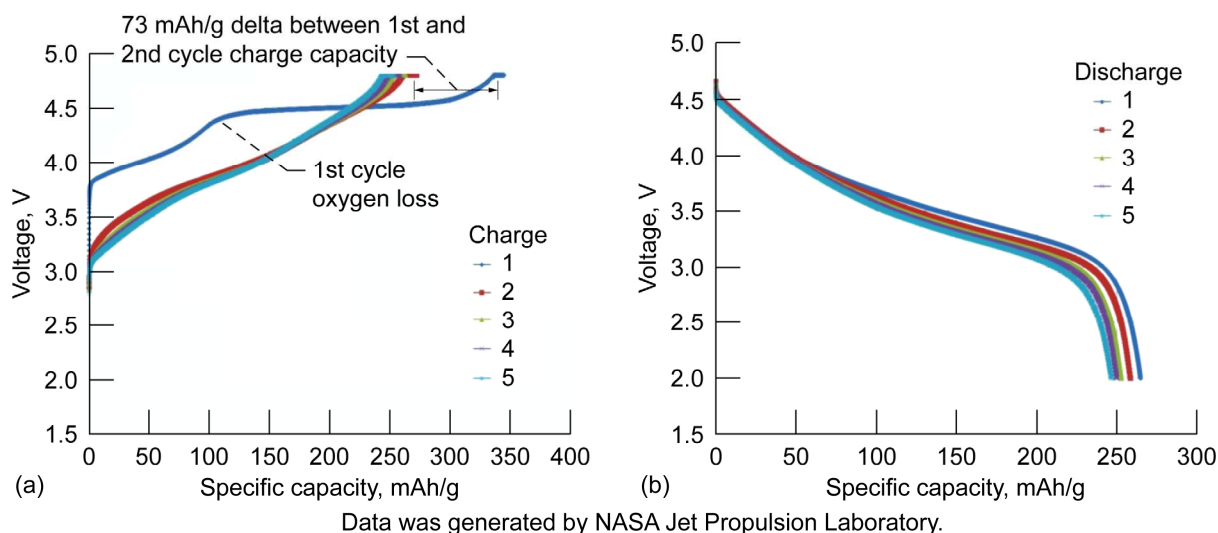


Figure 4.—Formation cycles for NEI Corporation LNMCO₂ cathode materials. (a) Charge cycles at C/20. (b) Discharge cycles at C/20.

In summary, we have achieved a specific capacity of 252 mAh/g to a 3.0 V cut-off at room temperature with our developmental cathodes. Higher specific capacity, better performance at low temperatures, and lower first cycle irreversible capacity are needed to achieve the project's goals. Additionally, improvements in tap density are required so that the cathode powders are suitable for manufacturing into practical electrodes.

2.2 Electrolytes

The objective of the electrolyte component development effort is to develop non-flammable or flame-retardant electrolytes that are stable up to 5 V while maintaining electrochemical performance (Refs. 21 to 29). Typical Li-ion cell electrolytes consist of a Li salt contained in organic carbonate solvents and are highly flammable. Under nominal operation, traditional Li-ion cells operate no higher than 4.2 V. Electrolyte systems for these cells are typically designed to be stable up to about 4.5 V (Ref. 29). Above this voltage, the electrolyte can begin to decompose and oxidize. Viability of the developmental electrolyte over a wider voltage window is essential, since the developmental cathodes will operate up to about 4.8 V to yield higher specific energy. The electrolytes are also required to offer good cycle life characteristics and enable good rate capability between 0 and 30 °C.

Technology challenges include the development of an electrolyte that is stable up to 5.0 V. To achieve this, different electrolyte formulations are combined with additives that have the capability to improve high voltage stability. Electrolyte additives that have properties known to improve interfacial characteristics at the electrolyte/electrode interface (solid-electrolyte-interface, or SEI) are also being explored to improve the electrolyte compatibility with the electrodes. Electrochemical interactions between the electrolyte and both electrode interfaces are investigated to assess this compatibility.

An additional challenge is to develop electrolytes that are non-flammable or flame retardant. Additives that possess known flame-retardant properties are combined with traditional Li-ion cell organic electrolytes. Flame retardant assessments are then performed on electrolytes that exhibited suitable electrochemical performance. Since the combination of both high-voltage stability and flame-retardance is required in one electrolyte system, successful flame retardant additives are combined with electrolytes that demonstrated high voltage stability.

Table 2 shows the results of flammability tests performed at the University of Rhode Island on six electrolytes. The self-extinguishing time (SET) for each electrolyte is shown. SET is defined as the time it takes for a cotton ball wick soaked with a fixed mass of electrolyte and ignited to burn itself out (Ref. 30). An organic electrolyte, 1.0M LiPF₆ in ethylene carbonate:ethyl methyl carbonate (EC:EMC) 30:70 by volume, was used as a baseline electrolyte for this set of tests to serve as a control. The control electrolyte, which contains no flame-retardant additives, burned for 33.4 s. The other five electrolytes, which were developed by Yardney Technical Products or NASA Jet Propulsion Laboratory, contain 5 to 20 percent flame-retardant additive content. Electrolytes containing flame-retardant additives exhibited SETs of between 0.4 to 22.45 s. These test results are not necessarily representative of the burn-time of a larger quantity of electrolyte in an actual cell, however they provide an indication of the relative burn time of one electrolyte formulation as compared to another. It should also be noted that since the mass of each electrolyte sample tested was fixed, the samples did not all contain the same amount of flammable components.

TABLE 2.—SELF-EXTINGUISHING TIMES OF DEVELOPMENTAL ELECTROLYTES
[Data was generated by the University of Rhode Island.]

Description	Electrolyte	Percentage flame retardant additive	SET/s	Standard deviation
“Baseline” Electrolyte	1.0M LiPF ₆ in EC/EMC (3:7)	None	33.4	3.4
JPL GEN #1 Electrolyte	1.0M LiPF ₆ in EC/EMC/TPP (2:7.5:0.5) + 2% VC	5% TPP	22.45	2.3
JPL Electrolyte	1.0M LiPF ₆ in EC/EMC/TPP (2:7:1) + 2% VC	10% TPP	9.57	0.9
JPL Electrolyte	Salt and carbonate blend	15% TPP	3.78	1.2
Yardney/URI GEN #2 Electrolyte	1.0M (95% LiPF ₆ + 5% LiBOB) in EC/EMC/DMMP (3/5.5/1.5)	15% DMMP	1.8	1.5
Yardney/URI GEN #1 Electrolyte	1.0M (95% LiPF ₆ + 5% LiBOB) in EC/EMC/DMMP (3/5/2)	20% DMMP	0.4	0.4

A final challenge is to produce electrolytes that possess the physical properties to ensure adequate conductivity and compatibility with the other cell components, including the electrodes and the separator. In addition to observing the results from the investigations above, care is taken to ensure that the electrolytes are not excessively viscous so that they can offer high ionic conductivity over the desired temperature range (high viscosity inhibits ion mobility). The ability of the electrolyte to effectively wet the separator is also tested to ensure its adequacy.

The experimental electrolytes are incorporated into electrochemical cells and cycled to an upper voltage cut-off of 4.8 V to investigate the impacts on rate capability, specific energy, energy density, and cycle-life. The experimental electrolytes should provide comparable life characteristics to a standard Li-ion cell electrolyte. It is expected that there will be some performance impact resulting from the use of an electrolyte system containing additives to improve the high-voltage stability and provide flame-retardant properties of the electrolyte. The benefits the advanced electrolyte offers must be balanced with any performance impacts that may result. Some results are discussed in Smart, et al. (Ref. 24).

2.3 Safety Components

Components are under development to enhance the inherent cell-level safety of the HE and UHE systems. Safe electrolytes and Li[LiNMC]O₂ cathodes, which have inherently higher thermal stability than SOA cathodes, were discussed above. Through contracts with independent research companies, NASA is also pursuing two approaches that are integrated within the electrodes in order to enhance the cell-level safety. SOA Li-ion battery systems rely on instrumentation and controllers to prevent unsafe

conditions that can be caused by improper operation or abuse of the battery. NASA's safety goals for the advanced HE and UHE cells dictate a need for cell-level technologies that are tolerant to electrical and thermal abuse such as over-temperature, overcharge, reversal, external short-circuit, and internal-shorts (meaning the cells pass simulated internal short circuit tests) with no fire or thermal runaway.

One approach to produce safer electrodes utilizes a cathode coating. Cobalt phosphate nanoparticles are prepared and are applied to the surface of metal oxide cathode particles using a thermal treatment (Refs. 31 to 33). This results in the formation of a lithium cobalt phosphate (LiCoPO_4) layer that encapsulates the cathode particles. Since LiCoPO_4 coating is a Li^+ ion conductor, the contact between the LiCoPO_4 and the cathode particle allows for rapid electron and Li^+ ion diffusion.

Metal phosphate cathodes are more thermally stable than metal oxide cathodes. As such, this approach has the potential to shift the cathode's exothermic peak to a higher temperature, and hence, greatly reduce or eliminate the potential for thermal runaway associated with the cathode component. The coating has successfully been demonstrated to eliminate the exothermic peak on SOA LiCoO_2 cathode materials (Ref. 32). Work is underway to incorporate the coating with different variants of $\text{Li}[\text{LiNMC}]\text{O}_2$ cathode materials to determine its applicability to these materials as well.

Another approach to producing safer electrodes involves a concept that can potentially shut-down reactions at the electrode surface. A coating consisting of a "composite thermal switch" is applied to either current collector, which is then coated with electrode material (Ref. 34). The goal is for the "switch" to increase the resistance of the electrode upon an increase in temperature above about $110\text{ }^\circ\text{C}$, such that the flow of current is terminated. This switch would conceivably be resettable for a limited amount of cycles, so that if the fault condition no longer exists, the switch would reverse and the cell could still function. The number of resettable cycles will be engineered to only a few, to mitigate any issues that a recurring unsafe condition might propagate.

As with the electrolytes, one of the keys to the successful implementation of a safety component into a cell is measured by its ability to reside within the cell with minimal impact on the overall cell performance. In the case of safety components, they may not necessarily be electrochemically active devices, they may occupy mass or volume in the system, and they may adversely impact conductivity or other cell electrical or electrochemical dynamics. The extent of which these components may impact practical performance must be evaluated in a full-cell configuration.

2.4 Separators

Commercial and developmental separators are being assessed to identify materials that are compatible with the cell chemistries that are under development and that provide an increased level of safety over SOA Li-ion cell separators. While the separator does not actively participate in the cell reaction, its function and reliability are critical to ensure the optimal electrochemical operation of the cell and its safety.

The separator acts as a physical barrier to prevent internal short-circuits between the anode and the cathode, however, its presence adds resistance to the cell. The design of separator materials must be optimized for low ionic resistance. High porosity generally facilitates high ionic conductivity. Simultaneously, the degree of porosity must be controlled to maintain mechanical strength.

Candidate separators should ideally also have the ability to shut-down cell reactions, and thus, the flow of current, above a specified temperature ($> \sim 130\text{ }^\circ\text{C}$) if overheating in the cell occurs. They should also retain their mechanical integrity at elevated temperatures to prevent a thermal runaway situation. Material assessments include the observation and measurement of physical, thermal, electrical, and mechanical properties. Desirable characteristic and properties for candidate separator materials are discussed in Reference 35 and procedures for characterizing and evaluating these materials are discussed in Reference 36. Assessment results of some of the materials under consideration are discussed in Reference 37.

3.0 Ultra High Energy Cell

The UHE cell will consist of components under development for the HE cell plus an advanced anode chemistry. Components used in the HE cell will continue to be developed for an additional year to maximize specific energy and other performance parameters before integration into the UHE flightweight cell. Potential issues with integration or compatibility of components will also be addressed during this timeframe.

3.1 Anodes

The component-level goal for the specific capacity of the advanced anodes is 1000 mAh/g when measured at C/10 and 0 °C. SOA carbonaceous anodes deliver about 320 to 350 mAh/g at C/10 and room temperature. Approximately a three-fold increase in specific capacity over SOA is required for the anode operating at like conditions. Silicon (Si) has a theoretical capacity of 4200 mAh/g, (~3600 mAh/g in the amorphous phase), however, practical attempts to create anodes from Si have led to the development of Si-composite materials that incorporate conductive carbons. The theoretical capacity of these composite materials is somewhat less than pure Si, but well above the stated capacity requirements. Technology development is being pursued to create practical anode materials that meet or exceed the specific capacity goals, and to achieve this sustainably (Refs. 38 to 40).

Current technology challenges associated with Si-based anode materials include accommodation or minimization of volume expansion during cycling and minimization of irreversible capacity loss. As a Li-ion cell containing a Si anode is cycled, Si particles expand by up to 400 percent as Li is alloyed. This results in isolation of the active material via particle detachment or fracture of the electrode, which leads to rapid capacity fade and poor coulombic efficiency (Ref. 41). An example of the irreversible capacity losses associated with these materials is shown in Figure 5. It shows a plot of the formation cycles for a

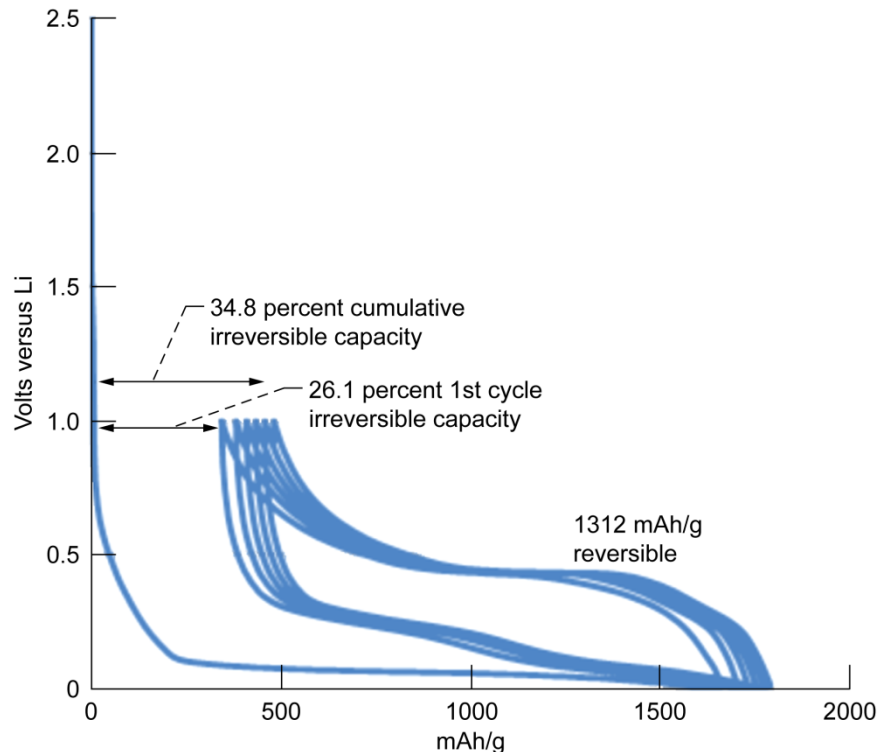


Figure 5.—First six cycles of a half cell with Si-C electrode versus Li/Li⁺ counter electrode.

half-cell with a Georgia Tech Research Corporation (GTRC) Si-C composite anode developed under contract with NASA versus a Li counter electrode at a C/20 rate. Twenty-six percent irreversible capacity is seen in the first cycle. Through 5 cycles, a cumulative 34.8 percent irreversible capacity is observed.

Approaches to address volume expansion of the silicon that are being pursued include optimization of the anode structure to accommodate the increase in volume. To achieve this, nano-structured Si-graphite and Si-carbon (Si-C) matrices, Si-C gel microspheres, and Si-C nanofoam anode materials coupled with elastomeric binders are being formulated with the aim of absorbing mechanical strain. The structure of the material is engineered to allow for elastic deformation and, hence, improve mechanical integrity. The binder type and concentration are varied to optimize the microstructure of the resultant materials. The porous electrodes that are formed afford a higher degree of utilization of the ionic pathways to facilitate better electrical conductivity within the electrode.

For the UHE cell, at least 200 cycles at 100 percent DOD are required on the cell-level before the capacity degrades to 80 percent of the initial C/2 capacity. In order to enable the cell-level goals, the cycle life goal for anodes is 250 cycles. While this is a moderate amount of cycles when compared to that of SOA carbonaceous anode materials, this is a challenge for silicon-composite materials. The loss of contact with active particles that occurs as a result of volume expansion reduces the cycle life dramatically. Addressing the volume changes adequately and the improvement in mechanical integrity that will result will improve the cycle life of these materials. In addition, cycling parameters for the materials are being optimized to determine the ideal operational parameters in order to maximize cycle life.

Preliminary results of on-going NASA and partner efforts to develop anode materials are shown below (Refs. 38 to 40). Most of the materials exhibit initial specific capacity at C/10 that exceeds the goals. When charged at 23 °C and discharged at 0 °C, all of the material samples tested have excellent capacity retention, delivering between 94 to 98 percent of their 23 °C capacity. While results to date are promising, significant capacity fade is observed upon cycling, the materials display high irreversible capacity, and their coulombic efficiency is poor, ranging from 95 to 98.5 percent, as compared to >99.9 percent for typical Li-ion systems.

Figure 6 shows specific capacity at 23 °C for two different materials developed for NASA at varying rates. Tests were performed in 2325-type coin cells with a Li-metal counter electrode, an electrolyte formulation of 1.0M LiPF₆ in EC:DEC:DMC in a 1:1:1 ratio by volume, and a Tonen Setela E20 separator. Each graph contains test results of replicate cells containing samples from the same electrode. The variability in capacity from cell-to-cell is attributed to variation in consistency in the handmade electrodes and to errors in precision when measuring the relatively small contribution of mass of the active material as compared to the mass of the current collector.

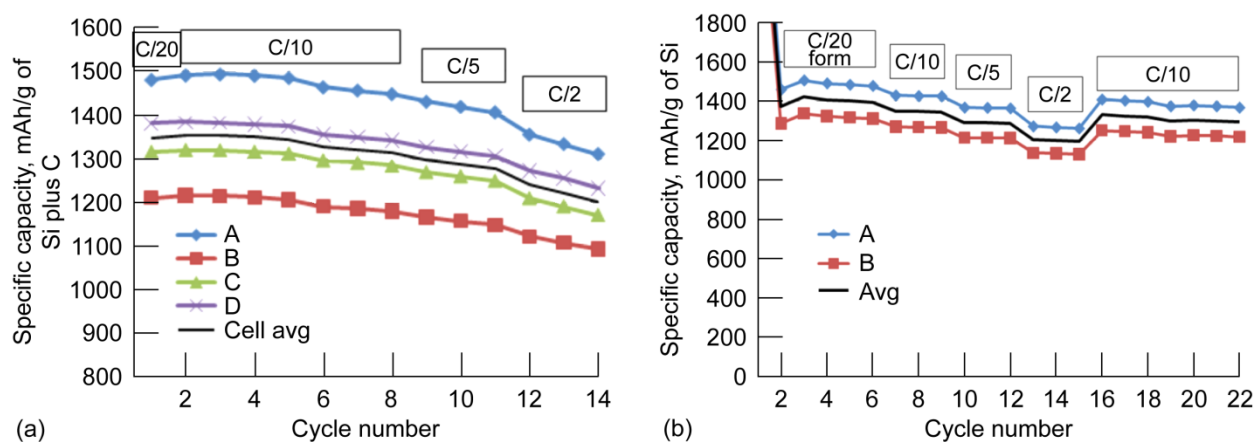


Figure 6.—Room temperature specific capacity at different rates in half cells with Li metal electrodes. (a) GTRC. (b) LMSSC.

Formation procedures and voltage limits for cycling were established individually for each material formulation based upon experimentation, due to their varied compositions and differing percentages of electrochemically active materials. Formation for materials synthesized by GTRC consists of one cycle at C/20 followed by four cycles at C/10. For all cycling, cells containing these materials were cycled between 1.0 V and 10 mV, with a C/50 taper charge. Formation for materials synthesized by Lockheed Martin Space Systems Company (LMSSC) under contract with NASA consists of five cycles at C/20. On the first formation cycle, cells were charged from 0.9 V versus Li to 25 mV, with a C/50 taper. For all subsequent cycling, the cut-off voltage on charge was limited to 170 mV with a C/50 taper. Formation and cycling procedures for LMSSC materials were largely based on work by Obravac (Ref. 42).

The highest specific capacity cell containing GTRC materials delivered an average of 1456 mAh/g over three cycles at C/10 (Cell A). The lowest specific capacity cell containing the same materials delivered an average of 1186 mAh/g (Cell B). The average C/10 capacity for all four cells was 1320 mAh/g. The rate of capacity fade increased slightly with increasing discharge rate. These materials retained an average of 97.6 and 92.5 percent of their C/10 capacity at C/5 and C/2, respectively. Empirical results are given in Table 3.

TABLE 3.—SPECIFIC CAPACITY OF SI-C COMPOSITE ANODES AT C/10 AND PERCENT OF C/10 CAPACITY DELIVERED AT DIFFERENT RATES: A) GTRC, AND B) LMSSC

	C/10	C/5		C/2		Final C/10	
Cell	Specific capacity (mAh/g of Si plus C)	Specific capacity (mAh/g of Si plus C)	Percent of C/10 capacity	Specific capacity (mAh/g of Si plus C)	Percent of C/10 capacity	Specific capacity (mAh/g of Si plus C)	Percent of initial C/10 capacity
A	1456	1418	97.4%	1332	91.5%	1336	91.8
B	1186	1157	97.6%	1107	93.4%	1095	92.3
C	1290	1260	97.6%	1190	92.2%	1190	92.2
D	1349	1317	97.6%	1253	92.9%	1246	92.3
Average	1320	1288	97.6%	1221	92.5%	1217	92.2

a) GTRC

	C/10	C/5		C/2		Final C/10	
Cell	Specific capacity (mAh/g of Si)	Specific capacity (mAh/g of Si)	Percent of C/10 capacity	Specific capacity (mAh/g of Si)	Percent of C/10 capacity	Specific capacity (mAh/g of Si)	Percent of initial C/10 capacity
A	1428	1367	95.7%	1268	88.8%	1404	98.3%
B	1268	1214	95.7%	1134	89.4%	1248	98.4%
Average	1348	1290	95.7%	1201	89.1%	1326	98.3%

b) LMSSC

Over three cycles at C/10, LMSSC materials delivered an average of 1428 mAh/g in Cell A and an average of 1268 mAh/g in Cell B. The average C/10 capacity for the two cells was 1348 mAh/g. These materials did not exhibit any appreciable increased rate of fade with increasing discharge rate, however, when cycled at different rates, the LMSSC material retained less of its C/10 capacity than the GTRC material. When returned to C/10 cycling on the tenth cycle after cycling at higher rates, the average C/10 capacity was greater than 98 percent of the initial C/10 capacity for both cells containing the LMSSC materials (see Table 3).

After rate capability testing, cycling continued on the GTRC and LMSSC materials to observe capacity retention during continuous cycling. As shown in Figure 7, the GTRC materials delivered 17 cycles and the LMSSC materials delivered 32 cycles to 80 percent of their initial C/10 capacities.

Future anode development efforts for the UHE cell will continue to focus on improving capacity fade, irreversible capacity loss, and coulombic efficiency. Consideration of a new anode material for the UHE cell presents a different set of challenges for the development of a new cell chemistry than for the HE cell, in which a new cathode is combined with a traditional anode. Alternative cathodes for Li-ion cells have been commercialized and materials suppliers and battery companies have a wide array of experience with

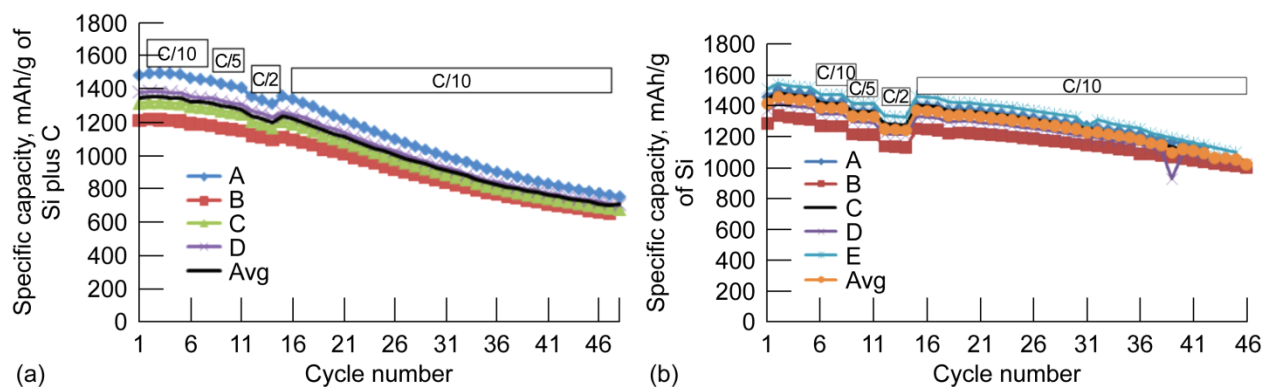


Figure 7.—Comparison of capacity fade for two Si-C composite anode materials through >45 cycles. (a) GTRC. (b) LMSSC.

the manufacture and processing of different cathode materials. However, the vast majority of commercial Li-ion cells, including those used for aerospace and military applications, utilize a carbonaceous anode, such as graphite, hard carbon, or meso-carbon microbeads (MCMB). Utilizing a radically different anode material can pose unexpected component integration issues, scale-up issues, and may possibly require the development of new manufacturing processes. The steps NASA is taking to address scalability and manufacturability of advanced materials, including the anodes, integration of components, cell-level safety, cell-matching, and any other issues that may arise early in the development process are discussed in References 43 and 44.

4.0 Summary

As this report describes, components for the HE and UHE cells are in various stages of development and have challenges that must be successfully addressed before the components are mature enough to be integrated into practical cells. In parallel with the individual component development efforts, components are matched up with other components for integration in laboratory cells to study their interactions and compatibility with one another. Also in parallel, components are being evaluated for their manufacturability and their ability to adapt to use in a production-scale environment. Once components are mature enough for integration into production-level cells, evaluation cells of a nominal 10 Ah capacity will be fabricated using combinations of developmental materials to study their performance and safety in a higher capacity, production format cell. The best combination of materials will be determined based on the performance of the evaluation cells. These materials will then be downselected for integration into flightweight cells.

Appendix—Abbreviations

Al ₂ O ₃	aluminum oxide
AlPO ₄	aluminum phosphate
°C	degrees Celsius
C	carbon
ConOps	Concept of Operations
DC	direct current
DEC	diethyl carbonate
DMC	dimethyl carbonate
DOD	depth-of-discharge
EC	ethylene carbonate
EMC	ethyl methyl carbonate
ETDD	Enabling Technology Development and Demonstration
ETDP	Exploration Technology and Development Program
EVA	extravehicular activities
FY	fiscal year
g/cc	grams per cubic centimeter
GTRC	Georgia Tech Research Corporation
HE	High Energy
HESPS	High Efficiency Space Power Systems
KPP	Key Performance Parameters
LiCoO ₂	lithium cobalt oxide
LiCoPO ₄	lithium cobalt phosphate
Li-ion	lithium-ion
LiPF ₆	lithium hexafluorophosphate
LMSSC	Lockheed Martin Space Systems Company
LNMCO ₂	lithium nickel manganese cobalt oxide
LSS	Lunar Surface Systems
M	molar
mAh/g	milliampere-hours per gram
MCMB	meso-carbon microbeads
mV	millivolts
NASA	National Aeronautics and Space Administration
NEO	Near Earth Object
PUP	portable utility pallet
RuO ₂	ruthenium oxide
SEI	solid electrolyte interface
SET	self-extinguishing time
Si	silicon
Si-C	silicon-carbon
SOA	state-of-the-art
UHE	Ultra High Energy
V	volts

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14. ABSTRACT Vehicles and stand-alone power systems that enable the next generation of human missions to the Moon will require energy storage systems that are safer, lighter, and more compact than current state-of-the-art (SOA) aerospace quality lithium-ion (Li-ion) batteries. NASA is developing advanced Li-ion cells to enable or enhance the power systems for the Altair Lunar Lander, Extravehicular Activities spacesuit, and rovers and portable utility pallets for Lunar Surface Systems. Advanced, high-performing materials are required to provide component-level performance that can offer the required gains at the integrated cell level. Although there is still a significant amount of work yet to be done, the present state of development activities has resulted in the synthesis of promising materials that approach the ultimate performance goals. This report on interim progress of the development efforts will elaborate on the challenges of the development activities, proposed strategies to overcome technical issues, and present performance of materials and cell components.					
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